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Synthesis and Characterization of a Series of Binuclear Ruthenium Complexes Bridged by 2,5-Pyrazine Dicarboxylate

DIANA SEDNEY and ANDREAS LUDI*

Institut für Anorganische Chemie, Universität Bern, CH-3000 Berne 9, Switzerland

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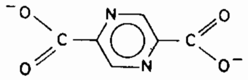
The preparation and chemical properties of the binuclear complexes $[(NH_3)_4RuLRu(NH_3)_4]^{2+,3+,4+}$, $[(NH_3)_4RuLRu(bipy)]^{3+,4+}$ *and* $[(bipy)_2RuLRu(bipy)_2]^{2+}$ *(L = 2,5-pyrazine dicarboxylate) are described along with the characterizations of the monomeric precursors. The visible absorption spectra of these complexes are dominated by intense* ($\epsilon > 4500$) *metal-to-ligand charge transfer bands. Electrochemical measurements suggest that the mixed valence* ($n = 3+$) *species should be stable towards disproportionation in all three cases. Low intensity* ($\epsilon < 450$) *intervalence transfer bands observed in the near infrared absorption spectra of the 3+ ions of the first two complexes demonstrate the weak metal–metal interactions of these mixed valence ions. No such band was found for the symmetric bis-bipyridyl dimer.*

Introduction

Since the first report of the synthesis of the now famous Creutz–Taube complex $[(NH_3)_5Ru\text{-pyrazine-}Ru(NH_3)_5]^{5+}$ [1], a number of mixed valence binuclear ruthenium complexes have been reported in the literature [2–5]. A characteristic of all these compounds is a bridging ligand which occupies a single coordination site of each component Ru atom. This paper presents the preparation and chemical characterization of a series of binuclear ruthenium complexes where the bridging ligand is the dianion 2,5-pyrazine dicarboxylate (dcpy):



This ligand ideally possesses C_{2h} symmetry which includes an inversion center. Its planarity and aromaticity have previously prompted an investigation of transition metal complexes and polymers of dcpy as potential semiconductors [6]. Another interesting feature of this ligand is its two negative charges. The net charges of the binuclear species discussed below are therefore lower than the charges typically found in complexes possessing uncharged nitrogen heterocyclic ligands.

Experimental

Preparation of Complexes

2,5-Pyrazinedicarboxylic acid

The diacid (H_2dcpy) was prepared from 2,5-dimethylpyrazine (Fluka) according to the method of Stoehr [7]. Due to the limited solubility of the diacid, the dipotassium salt (K_2dcpy) was used in the following syntheses.

$[Ru(bipy)_2(Hdcpy)](PF_6)\cdot H_2O$, *I*

451 mg of K_2dcpy (1.85 mmol) were dissolved in 10 ml of deionized H_2O and were added to 441 mg of $Ru(bipy)_2Cl_2\cdot 2H_2O$ [8] (0.85 mmol) in 30 ml of EtOH/H_2O (2:1). This solution was refluxed for six hours. A spot test on a silica gel TLC plate showed that the brown solution contained an orange and a green component. Addition of 2 ml of 0.5 *M* NH_4PF_6 induced precipitation of the green component which was collected by filtration. The orange filtrate was purified by elution from a cellulose–silica gel column (15 cm cellulose over 2 cm silica gel in a column 2 cm in diameter). Elution was achieved with H_2O and a green band could be eluted with 5% acetic acid. The orange eluate was filtered, reduced in volume and the pH adjusted to between 3 and 4 with 1 *M* HCl. After the addition of 2 ml of 0.5 *M* NH_4PF_6 the orange solution was allowed to slowly evaporate in a crystallizing dish. After a few days, small, dark orange, triclinic (a = 7.37 Å, b = 9.04 Å, c = 17.86 Å; α = 122°38′, β = 137°30′, γ = 66°36′) crystals with a green metallic luster had formed. These crystals were washed with very small portions of ice cold H_2O, followed by ether and were air dried. *Anal.* Calcd for $[Ru(C_{10}H_8N_2)_2(C_6H_3N_2O_4](PF_6)\cdot$

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*Author to whom correspondence should be addressed.

H_2O: C, 42.0; H, 2.85; N, 11.3; F, 15.3. Found: C, 42.3; H, 3.0; N, 11.4; F, 15.4.

[(bipy)₂RudcpyRu(bipy)₂](PF₆)₂·3H₂O, II

The green precipitate described in the synthesis of I was found to be the binuclear species II. This precipitate was recrystallized by dissolving in 0.01 *M* HCl, reducing the volume to a few milliliters and reprecipitating with NH_4PF_6. *Anal.* Calcd for $[Ru_2(C_{10}H_8N_2)_4(C_6H_2N_2O_4)](PF_6)_2\cdot 3H_2O$: C, 41.3; H, 3.02; N, 10.5. Found: C, 41.5; H, 3.1; N, 10.5.

[Ru(NH₃)₄(Hdcpy)] Cl·3H₂O III

156.5 mg of *cis*-$[Ru(NH_3)_4Cl_2]Cl$ [9] (0.57 mmol) in 8 ml of deionized H_2O was reduced over a Zn/Hg amalgam in an argon stream. The yellow solution was then added to 421 mg of K_2dcpy (1.73 mmol) producing a deep purple solution. This solution was stirred under argon for four hours. At the end of this period 2 ml of 1 *M* HCl was added to precipitate any free ligand. After filtering, a navy blue precipitate was obtained by adding a threefold volume of ethanol. The solid product was purified by recrystallization from 1 *M* HCl and EtOH. *Anal.* Calcd for $[Ru(NH_3)_4(C_6H_3N_2O_4)]Cl\cdot 2H_2O$: C, 17.7; H, 4.7; N, 20.6; Cl, 8.7. Found: C, 18.3; H, 4.6; N, 20.4; Cl, 8.4.

[(NH₃)₄RudcpyRu(NH₃)₄] Cl₂·H₂O, IV

Synthesis of this binuclear complex proceeds as described for III using stoichiometric amounts of *cis*-$[Ru(NH_3)_4Cl_2]Cl$ and K_2dcpy (2:1). Deionized H_2O is used in place of 1 *M* HCl in the precipitation and recrystallization steps. *Anal.* Calcd for $[Ru_2(NH_3)_8(C_6H_2N_2O_4)]Cl_2\cdot H_2O$: C, 11.8; H, 4.9; N, 22.9. Found: C, 11.7; H, 4.8; N, 22.2.

[(NH₃)₄RudcpyRu(NH₃)₄](PF₆)₃·xH₂O, V

Complex IV was dissolved in a few milliliters of deionized H_2O. A cerium (IV) solution was added dropwise until the solution was blue in color. NH_4PF_6 was added and the volume of the solution was reduced. A blue precipitate was recovered upon the addition of ethanol. The product was purified by dissolving in H_2O and reprecipitating with ethanol. Purity was confirmed by comparing extinction coefficients of the charge transfer bands with ϵ for the one electron oxidation product of IV.

[(NH₃)₄RudcpyRu(bipy)₂](PF₆)₃·H₂O, VI

114 mg of I (0.15 mmol) and 109 mg of $[Ru(NH_3)_4(H_2O)_2](PF_6)_2$ [9] (0.22 mmol) were placed in a foil covered Schlenk vessel. Ten ml of deaerated acetone were added and the solution was stirred under argon for six hours. A blackish precipitate was observed at the end of this time. Precipitation was enhanced by the addition of $[(t\text{-}Bu)_4N]PF_6$ dissolved in 1 ml of acetone. After chilling for ½ hour, the solid product was collected by filtration, recrystallized from acetone, washed with ether and air dried. An alternative synthesis was carried out in aqueous solution. $[Ru(NH_3)_4(H_2O)_2]^{2+}$ was prepared *in situ* by reducing *cis*-$[Ru(NH_3)_4Cl_2]Cl$ as described for III and adding a stoichiometric quantity of I. Although the mononuclear precursors are Ru(II) complexes, the product recovered contains equimolar Ru(II) and Ru(III). A 3+ charge was verified by ion exchange (Dowex 50 resin) as well as by elemental analysis. *Anal.* Calcd for $[Ru_2(NH_3)_4(C_{10}H_8N_2)_2(C_6H_2N_2O_4)](PF_6)_3\cdot H_2O$: C, 26.0; H, 2.68; N, 11.7. Found: C, 26.1; H, 3.0; N, 12.1.

Physical Methods

Ultraviolet–visible absorption spectra were recorded on a Beckman 24 spectrophotometer and a Beckman DK2 was used in the near infrared region. All spectra are reported for solutions at room temperature. Infrared spectra were obtained with KBr pellets using a Perkin-Elmer 580 spectrophotometer. Cyclic voltammograms were scanned using $\sim 10^{-4}$ *M* solutions in either 0.1 *M* KCl/0.001 *M* HCl or 0.1 *M* $[(t\text{-}Bu)_4N](PF_6)$ in acetonitrile. A platinum foil working electrode was referenced against SSCE or Ag/Ag^+ (0.01 *M*) electrodes. Potentiometric pK_A measurements employed a standard glass electrode (Metrohm) *versus* a Ag/AgCl reference electrode and were carried out in 1 *M* KNO_3 at 25 °C. In a typical experiment, a 10^{-3} *M* sample dissolved in 10^{-2} *M* HNO_3/1 *M* KNO_3 was titrated with 10^{-2} *M* NaOH/1 *M* KNO_3. The pK_A values were calculated as a function of $[H^+_{bound}]/[complex]_{total}$ and pH according to the Newton–Raphson iterative procedure [10]. Proton NMR spectra were run on a Varian XL–100 instrument. The unit cell of $[Ru(bipy)_2(Hdcpy)](PF_6)\cdot H_2O$ was determined from precession photographs. Microanalyses were performed by Ciba-Geigy microanalytical laboratory in Basel.

Results and Discussion

Absorption Spectra

The visible spectra of compounds I through VI are shown in Figs. 1–3. Table I provides a summary of their spectral features. Comparison of the positions and intensities of the bands between 400 and 750 nm with other bis(bipy) [11, 12] and tetraammine [13] Ru(II) complexes containing heterocyclic ligands identifies these bands as metal-to-ligand charge transfer (MLCT) bands.

For the tetraammine complexes, a substantial shift of these bands to lower energy is observed upon dimerization (Fig. 1). Comparing the spectrum of III with IV, the low energy band maxima differ by 3500 cm^{-1} and the high energy bands by 3070 cm^{-1}.

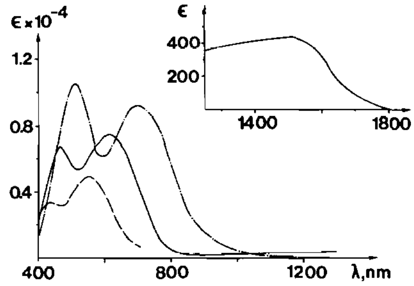


Fig. 1. Visible spectra of $[Ru(NH_3)_4(Hdcpy)]^+$ (III) (– – –), $[(NH_3)_4RudcpyRu(NH_3)_4]^{2+}$ (IV) (–·–·–) and $[(NH_3)_4RudcpyRu(NH_3)_4]^{3+}$ (V) (———) in H_2O. The near infrared spectrum of V in D_2O is shown in the inset.

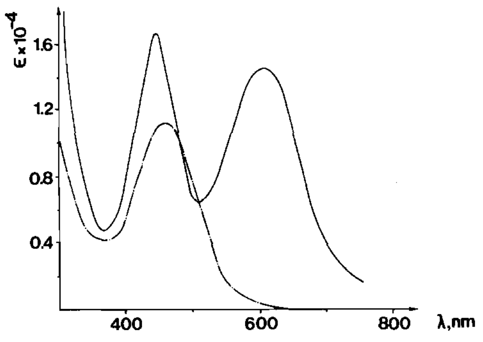


Fig. 2. Visible spectra of $[Ru(bipy)(Hdcpy)]^+$ (I) (–·–·–) and $[(bipy)_2RudcpyRu(bipy)_2]^{2+}$ (II) (———) in H_2O.

This red shift can be attributed to a combination of electrostatic and π-backbonding effects. The addition of an 'acidic' moiety ($[Ru(NH_3)_4]^{2+}$ in this case) to a heterocyclic bridge has been shown to cause a decrease in the MLCT energy [14, 15].

However, this cannot be the sole factor in producing the observed shift to lower energy in the dimer, since oxidation of one Ru(II) unit to Ru(III) does not cause a further decrease in the energy of the charge transfer bands. The second $[Ru(NH_3)_4]^{2+}$ moiety is more than a simple 'acidic' center; it can also participate in dπ → π* backbonding producing a decrease in the energy of the ligand π* level. This decrease is also reflected in the ligand π → π* transition. For the monomer III, the π → π* transition occurs at 253 nm. Upon dimerization, this band is shifted 2300 cm^{-1} lower in energy to 269 nm.

The predominance of the backbonding over the electrostatic contribution can be seen by comparing the spectrum of IV with that of V. The observed hypsochromic shift for the mixed valence complex results from the decreased overlap of the Ru(III) *versus* Ru(II) dπ orbitals with the ligand π* system.

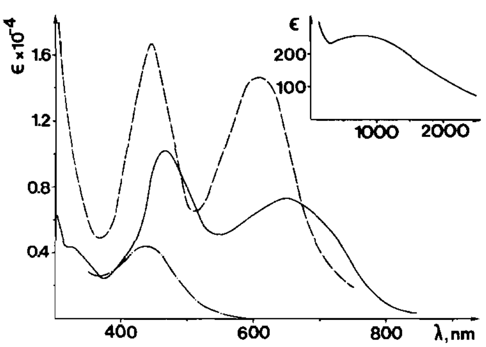


Fig. 3. Visible spectrum of $[(NH_3)_4RudcpyRu(bipy)_2]^{3+}$ (VI) (———) in H_2O. The near infrared spectrum of VI in DMSO is shown in the inset. The spectra of II (– – –) and $[(NH_3)_4RudcpyRu(NH_3)_4]^{4+}$ (–·–·–) in H_2O are shown for comparitive purposes.

A similar mechanism may be responsible for the appearance of a new band in the bis-bipyridyl dimer II (Fig. 2). The dπ → π* (dcpy) transition cannot be distinguished from the dπ → π* (bipy) transition in the monomer but the energy of the dπ → π* (dcpy) band would be expected to decrease in the dimer. This phenomena has also been observed for similar complexes where 2,2'-bipyrimidine is in the bridging ligand [16].

The spectrum of the asymmetric dimer VI appears to be a composite of II and $[(NH_3)_4RuddcpyRu(NH_3)_4]^{4+}$ (Fig. 3), as is typical of class II mixed valence complexes. The solvent dependence of the peaks at 652 and 473 nm parallels that of the MLCT bands in II. The higher energy band exhibits only slight solvent dependence as it slowly decreases in energy as solvent polarity decreases (as measured by the empirical Dimroth parameter E_T [17]). Opposite behavior is displayed by the low energy band. Here, the band position is strongly solvent dependent and the energy increases with decreasing polarity. This effect can be thought of as a stabilization of the dcpy LUMO as solvent polarity increases.

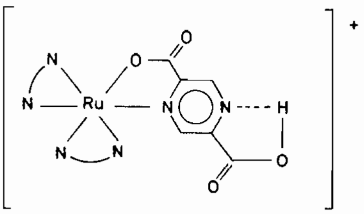
IR Spectra

The stretching frequencies of the carboxylate group are particularly useful in identifying these complexes. Compound I shows two ν(COO)(asym) bands, one at 1716 cm^{-1} and another at 1661 cm^{-1}. The higher energy band corresponds to a carboxylic acid function and the lower energy band is evidence for a Ru bound carboxylate, (compare with 1700 cm^{-1} for H_2dcpy and 1621 cm^{-1} for K_2dcpy). Also there are broad weak bands occurring around 1900 and 1500 cm^{-1} in I which are characteristic of intramolecular hydrogen bonding [18]. Thus, the following is proposed for I:

TABLE I. Spectral Data for Ru-pyrazinedicarboxylate Complexes in H_2O.

Complex	Text Designation	λ_{max}, nm	(ν_{max}, cm^{-1})	$\epsilon \times 10^{-4}$ M^{-1} cm^{-1}
$[Ru(bipy)_2(Hdcpy)]^+$	I	461	(21,700)	1.12
		286	(35,000)	10.0
$[Ru(bipy)_3]^{2+}$ [a]		452	(22,100)	1.46
		423 (sh)	(23,600)	
$[(bipy)_2RudcpyRu(bipy)_2]^{2+}$	II	605	(16,500)	1.38
		448	(22,300)	1.77
		286	(35,000)	
$[Ru(NH_3)_4(Hdcpy)]^+$	III	557	(18,000)	0.49
		435	(23,000)	0.34
		253	(39,500)	14.3
$[Ru(NH_3)_4(Hdcpy)]^{2+}$		637 (br)	(15,700)	0.03
		362	(27,600)	0.24
$[Ru(NH_3)_4picolinate]^+$ [b]		540	(18,500)	0.1
		386	(25,900)	0.1
$[(NH_3)_4RudcpyRu(NH_3)_4]^{2+}$	IV	748 (sh)	(13,400)	
		692	(14,500)	0.92
		502	(19,900)	1.04
		269	(37,200)	1.53
$[(NH_3)_4RudcpyRu(NH_3)_4]^{3+}$	V	610	(16,400)	0.76
		462	(21,600)	0.65
		275	(36,400)	1.35
$[(NH_3)_4RudcpyRu(NH_3)_4]^{4+}$		435	(23,000)	0.44
$[(NH_3)_4RudcpyRu(bipy)_2]^{3+}$	VI	652	(15,300)	0.73
		473	(21,100)	1.02
		332 (sh)	(30,100)	
		278	(36,000)	4.40

[a] Reference 11. [b] Reference 13.



No evidence of H bonding is observed in the IR spectrum of II and as expected for a symmetric dimer formulation there is a single ν(COO) (asym) band at 1652 cm^{-1}. The tetraammine monomer III also shows bands attributable to intramolecular hydrogen bonding (2400 cm^{-1} (m, br); 1900 (m, br); ν(COO) (asym): 1697 (m), 1649 (s)).

Cyclic Voltammetry

Formal reduction potentials for I through VI are listed in Table II. The reduction potentials are diagnostic of the degree of metal–ligand bridge–metal interaction that results upon formation of a dimer. Also K_{com}, the comproportionation constant, can be calculated from the $E_{1/2}$ values to determine the stability of mixed valence complexes [19].

TABLE II. Electrochemical Data.

Complex		$E_{1/2}$ [a], V (*vs.* NHE)
$[Ru(bipy)_2(Hdcpy)]^{2+,+}$		0.97b
$[(bipy)_2RudcpyRu(bipy)_2]^{3+,2+}_{4+,3+}$	(1)	0.98[b]
	(2)	1.16
$[Ru(NH_3)_4(Hdcpy)]^{2+,+}$		0.41[c]
$[(NH_3)_4RudcpyRu(NH_3)_4]^{3+,2+}_{4+,3+}$	(1)	0.32[c]
	(2)	0.62
$[(NH_3)_4RudcpyRu(bipy)_2]^{3+,2+}_{4+,3+}$	(1)	0.30[b]
	(2)	1.11

[a] Reported values are referenced against NHE using Ru-$(bipy)_3^{3+,2+}$ (1.26 V) and $Ru(NH_3)_6^{3+,2+}$ (0.05 V) as standards. [b] Measured in 0.1 *M* $[(t\text{-}Bu)_4N]PF_6$ – acetonitrile (Pt *vs.* Ag/Ag^+ (0.01 *M*)). [c] Measured in 0.001 *M* HCl/ 0.1 *M* KCl (Pt *vs.* SSCE).

The reduction potential of I is 0.29 V lower than $Ru(bipy)_3^{3+}$, *i.e.* the Ru(II) center in I is more readily oxidized than the tris-(bipy) complex. This reflects an increase in electron density on the Ru(II) atom due to the decreased π-backbonding capacity of dcpy *versus* bipy Little change occurs in the $E_{1/2}$ (1) value of I when compared to the monomer I Electrostatic effects predicted by the higher charge of the dimer are offset by the decrease in backbonding now that the π^* system of dcpy is shared by two ruthenium centers Such a decrease is more pronounced in the tetraammine complexes (III and IV) because here it is only the bridging ligand that is capable of backbonding

The difference between the first and second oxidation steps of II is 0 18 V which corresponds to a K_{com} of 1.1×10^3 The mixed valence complex $[(bipy)_2RudcpyRu(bipy)_2]^{3+}$ should therefore be quite stable In IV the two potentials are separated by 0 30 V resulting in a K_{com} of $1\ 2 \times 10^5$ For the asymmetric complex VI the two potentials can be assigned to the following couples $[(NH_3)_4Ru^{III}\text{-}dcpyRu^{II}(bipy)_2]^{3+} + e^- \rightarrow [(NH_3)_4Ru^{II}dcpyRu^{II}(bipy)_2]^{2+}$, $E_{1/2}$ (1) = 0 30 V $[(NH_3)_4Ru^{III}dcpy\text{-}Ru^{III}(bipy)_2]^{4+} + e^- \rightarrow [(NH_3)_4Ru^{III}dcpyRu^{II}\text{-}(bipy)_2]^{3+}$, $E_{1/2}$ (2) = 1 11 V These potentials correspond quite well to the first and second oxidation steps of IV and II respectively, suggesting that the degree of communication across the dcpy bridge is small Here, K_{com} is calculated to be $4\ 9 \times 10^{13}$ This large K_{com} is born out by experimental observation Although the preparation of VI begins with Ru(III) precursors, a 3+ salt is obtained upon precipitation with PF_6^- Typical K_{com}'s for other asymmetric binuclear Ru complexes of the type $[(NH_3)_5RuL\text{-}RuCl(bipy)_2]^{n+}$ are ~10^7 [3] The increased stability of VI may be a consequence of replacing the chloride ion in the Ru bis–(bipy) coordination sphere Consideration of the appropriate monomeric species illustrates this effect While $[Ru(NH_3)_4(Hdcpy)]^+$ is more easily oxidized than $[Ru(NH_3)_5pyrazine]^{2+}$ (0 41 *vs* 0 55 V), $[Ru(bipy)_2(Hdcpy)]^+$ is harder to oxidize than $[RuCl(bipy)_2pyrazine]^+$ (0.98 *vs* 0 88 V). If this analogy is carried to the dimeric complexes, the Cl^- serves to increase electron density on the Ru(II) center thus making the [3,3] complex more accessible in a disproportionation reaction The large K_{com} observed for $[(NH_3)_4Rubipyrimidine\text{-}Ru(bipy)_2]^{4+}$ ($\Delta E_{1/2}$ = 0 69 → K_{com} = $4\ 6 \times 10^{11}$) [16] lends further credence to this explanation

pK_A *Determinations*

Just as the reduction potentials monitor the changes in electron delocalization between monomeric and dimeric complexes, pK_A measurements contrast these changes between free ligands and monomers In the literature only a single pK_A value is reported for dcpy, 2 29 [20] The pK_A has been redetermined in this laboratory by potentiometric titration A value of 3 19 ± 0 13 [21] was calculated for pK_{A_2} Precipitation of the diacid below pH ~ 3 precludes an accurate evaluation of pK_{A_1}

Titration of I in both acidic and basic media (always in 1 *M* KNO_3) yields two distinct deprotonation steps corresponding to pK_{A_1} = 2 49 and pK_{A_2} = 9 52 In the low pH range, both the free carboxylate group and the pyrazine N appear to be protonated. The visible spectrum of I in acidic solution consists of two bands One band occurs at 447 nm with a second, quite broad band appearing around 480 nm. The variation in the spectra of the deprotonated *versus* the monoprotonated species is too slight to provide a precise determination of pK_{A_1} by the spectrophotometric method [15]. No change is seen in the spectra above pH 5

Complexation with the $[Ru(bipy)_2]^{2+}$ moiety increases the basicity of the free carboxylate group (and nitrogen, since a proton is shared by both entities) by ~6 pK_A units over the free ligand Lavallee and Fleischer [15] have ascribed the increase in basicity observed for $[Ru(NH_3)_5pyrazine]^{2+}$ compared with free pyrazine to the better charge delocalization capacity of the Ru(II) species. They also invoke proton chemical shift data to advance this explanation The NMR spectrum of I in D_2O follows the same shift patterns noted in their study Two distinct doublets at δ 8.33 and 9 14 (*vs* TMS) are attributable to the *ortho* and *meta* protons, respectively, (relative to the Ru bound N) of the dcpy ring The free ligand shows a single signal at δ 8 97 The upfield shift of 0 64 ppm for the *ortho* proton has been attributed to the influence of paramagnetic anisotropy (This explanation has also been offered by Malin *et al* [22] to explain the downfield shifts observed for the ortho ring protons in a series of $[Fe(CN_5)L]^{n-}$ (L = nitrogen heterocycles) complexes) The downfield shift of 0 17 ppm observed for the *meta* proton which is further from and therefore less affected by the Ru(II) atom is evidence of the increased positive charge at the *meta* carbon atom

Intervalence Transfer (IT)

When IV is oxidized with ½ mol of Br_2 per mol of dimer an absorption occurs in the near infrared region (NIR) (Fig 1) The intensity of this band at its maximum absorbance ($\epsilon_{1510\,nm}$ = 430 M^{-1} cm^{-1}) coupled with the fact that neither the [2,2] nor [3,3] complexes show any absorption in this region identify it as an intervalence transfer transition This absorption is unusual in two respects First, the peak rises quickly to a maximum on the low energy side If a Gaussian band shape were assumed (based on the absorption below 1560 nm and its mirror image) the band width ($\Delta\bar{\nu}_{1/2}$, full width at half height) is ~1000 cm^{-1} which is even narrower than $\Delta\bar{\nu}_{1/2}$ of the Creutz–Taube complex (~1600 cm^{-1}) The second noteworthy feature is the very slow decline in intensity on moving towards higher energy. This phenomena has not been observed in other reported IT bands [3–5, 14]. One explanation may be that a number of IT transitions become allowed through distortion of the nominal octahedral site symmetry upon introduction of the tetradentate bridge. Unfortunately, the complex is not sufficiently soluble in solvents other than D_2O to determine solvent effects. In addition, the lack of any regular shape precludes the use of the Hush formulas which are commonly used in calculating properties of the IT transition. The NIR spectrum is presented here simply as evidence for the assignment of complex V as a class II mixed valence complex.

A NIR band is also seen in the spectrum of VI (Fig. 3, inset). The intensity is quite low ($\epsilon \sim 250$) and the band energy (10,400 cm^{-1}) is typical of other asymmetric dimers [3]. The band is not detected in aqueous or acetonitrile solutions due to its proximity to the low energy MLCT band, but can be seen in DMSO. If a symmetric band shape is assumed, $\Delta\bar{\nu}_{1/2}$ is 3500 cm^{-1}. This value is in good agreement with the calculated $\Delta\bar{\nu}_{1/2}$ of 3400 cm^{-1} predicted by the Hush formula [23]:

$$\bar{\nu}_{op} - \bar{\nu}_o = (\Delta\bar{\nu}_{1/2})^2/2310$$

Here, $\bar{\nu}_{op}$ is 10,400 cm^{-1} and $\bar{\nu}_o$ is estimated to be ~5,500 cm^{-1} (0.68 V) [24]. The degree of delocalization, α^2, can also be calculated using the Hush formula:

$$\alpha^2 = \frac{(4.2 \times 10^{-4})\, \epsilon_{max}\, (\Delta\bar{\nu}_{1/2})}{\bar{\nu}_{max} d^2}$$

Using values of $\epsilon = 250\ M^{-1}\ cm^{-1}$, $\Delta\bar{\nu}_{1/2} = 3{,}500\ cm^{-1}$, $\bar{\nu}_{max} = 10{,}400\ cm^{-1}$ and d = 7 Å (the Ru–Ru distance is assumed to be comparable to the d determined for the Creutz–Taube complex), α^2 is calculated as 7.2×10^{-4}. The small α^2 could have been predicted from the close agreement of $\Delta\bar{\nu}_{1/2}$ (exp.) and $\Delta\bar{\nu}_{1/2}$ (calc.) since the Hush treatment loses validity as one moves away from the localized limit.

Contrary to the electrochemical evidence presented earlier, no mixed valence species corresponding to a formula $[(bipy)_2RudcpyRu(bipy)_2]^{3+}$ could be isolated. Near infrared spectra of solutions of II containing 1 mol of Ce(IV) per mol of dimer gave no indication of an IT transition. If the decrease in ϵ that occurs upon replacing the $[Ru(NH_3)_4]^{2+}$ unit in V with $[Ru(bipy)_2]^{2+}$ in VI may be considered as the beginning of a trend, the intensity of the IT transition of the proposed symmetric bis(bipy) mixed valence complex may be so low as to be unobservable. An alternative explanation may be that the band arising from an IT transition is sufficiently high in energy to be obscured by the tail of the low energy MLCT band.

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